(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 292 120 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 22.07.92 (51) Int. Cl.5: C08J 3/22

(21) Application number: 88303697.2

(22) Date of filing: 25.04.88

The file contains technical information submitted after the application was filed and not included in this specification

(54) Process for producing polyester resin composition.

(30) Priority: 23.04.87 JP 100917/87

(43) Date of publication of application: 23.11.88 Bulletin 88/47

(45) Publication of the grant of the patent: 22.07.92 Bulletin 92/30

(84) Designated Contracting States: DE FR GB IT NL

(56) References cited:
GB-A- 2 176 492
US-A- 4 309 374

INTERNATIONAL POLYMER SCIENCE AND TECHNOLOGY, vol 10, no 12, 1983, pages T63-T76, Shawbury, Shrewsbury, GB; S Suzuki 'Colour Masterbatches'

PATENT ABSTRACTS OF JAPAN, vol 10, no 120 (C-343)(2177), 6th May 1986

PATENT ABSTRACTS OF JAPAN, vol 11, no 101 (C-413)(2548), 31 March 1987

(73) Proprietor: KONICA CORPORATION
26-2, Nishishinjuku 1-chome, Shinjuku-ku
Tokyo 160(JP)

Proprietor: KANEBO, LTD.
17-4 Sumida 5-chome Sumida-ku
Tokyo 131(JP)

(72) Inventor: Kiyohara, Kazuto
c/o Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: Hagiwara, Toshiyuki
c/o Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: Nakadate, Takanori
c/o Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: Harada, Ichiya
c/o Konica Corporation 1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: Noguchi, Kentaro c/o Kanebo Ltd.
Hofu-Plant No. 4-1, Kanebo-chu
Hofu-shi Yamaguchi-ken 747(JP)
Inventor: Sakae, Shigeru c/o Kanebo Ltd.
Hofu-Plant No. 4-1, Kanebo-chu
Hofu-shi Yamaguchi-ken 747(JP)

EP 0 292 120 B1

Inventor: **Okuma, Kazuhiro c/o Kanebo Ltd.**
Hofu-Plant No. 4-1, Kanebo-chu
Hofu-shi Yamaguchi-ken 747(JP)

(74) Representative: **Ellis-Jones, Patrick George Armine et al**
J.A. KEMP & CO. 14 South Square Gray's Inn
London WC1R 5EU(GB)

Description

The present invention relates to a process for producing a titanium dioxide containing polyester resin composition which may, for example, be used in the preparation of a reflective photographic support.

White inorganic pigments typified by titanium dioxide are conventionally dispersed in polyester resins typified by polyethylene terephthalate (PET) by either adding such pigments per se or by suspending them in an ester-forming polyhydric alcohol such as ethylene glycol to prepare a slurry and adding the slurry during esterification or polycondensation. The latter method is disclosed in many prior patents such as Japanese Patent Publication Nos. 945/1958 and 18135/1981. However this method has the problems that the particles of titanium dioxide added tend to agglomerate and precipitate in ethylene glycol or the resulting polymer, and that the amount of titanium dioxide that can be incorporated is no more than several percent.

If it is desired to incorporate a fairly large amount (≥10%) of titanium dioxide in the polyester resin, it is common practice to knead the resin, for example in a continuous kneading extruder. Methods for adding titanium dioxide and other white inorganic pigments to polyester resins with a continuous kneading extruder are described in Japanese Patent Application (OPI) Nos. 246236/1986 and 250034/1986 (the term "OPI" means an unexamined published Japanese Patent Application). The method described in Japanese Patent Application (OPI) No. 246236/1986 comprises dry blending a pigment with a polyester resin having a bulk density of no more than 0.6, blending them in molten state to prepare a master batch, and mixing the master batch with another feed of the polyester resin in molten state. However, providing a polyester resin with a bulk density of no more than 0.6 and dry blending it with a pigment are quite cumbersome steps and the added pigment particles are frequently not uniformly dispersed in the resin.

The method disclosed in Japanese Patent Application (OPI) No. 250034/1986 comprises mixing a polyester resin with a pigment in molten state to prepare a master batch, subjecting the master batch to solid-phase polymerization, and mixing the resulting polymer with another feed of the polyester resin. This method has the following disadvantages: the polymerization requires as long as 5 to 20 hours to complete; the method involves many steps; and, as in the first method, the added pigment particles are sometimes not uniformly dispersed in the polyester resins. Furthermore, the two methods have a common problem in that the resin can pick up color as it is subjected to two cycles of blending in a molten state.

The present invention provides a process for producing a polyester resin composition by first supplying a polyester resin having an intrinsic viscosity of at least 0.40 and titanium dioxide having an average particle size of 0.1 to 0.5 µm and a water content of no more than 0.5%, the particles of which have been surface treated with an aluminum compound and/or a silicon compound, to a continuous kneading extruder, kneading them in the molten state such that the concentration of titanium dioxide is from 20 to 70 wt%, and then supplying an additional charge of the polyester resin to give a desired concentration of the titanium dioxide.

The process of the present invention provides a polyester resin composition having a high concentration of titanium dioxide dispersed uniformly, which composition can be produced in fewer steps and within a short period of time.

The continuous kneading extruder used in the process of the present invention may be of any type that permits continuous kneading and extrusion, such as an extruder equipped with a kneading rotor or blades, a corotating or counter-rotating twin-screw kneading extruder or a single-screw continuous kneader.

The polyester resin used in the present invention may of course be a thermoplastic resin solely composed of a polyester. Included within the scope of the "polyester resin" are blends of a polyester and other polymers or additives that are incorporated in such amounts that the resin characteristics of the polyester as the chief component will not be affected for practical purposes.

Polyester resins that can be used in the present invention are polymers of the condensation products of aromatic dicarboxylic acids (e.g., terephthalic acid, isophthalic acid, phthalic acid and naphthalenedicarboxylic acid) and glycols (e.g., ethylene glycol, 1,3-propanediol and 1,4-butanediol); examples are polyethylene terephthalate, polyethylene 2,6-dinaphthalate, polypropylene terephthalate, polybutylene terephthalate, and copolymers thereof. Polyethylene terephthalate (hereinafter abbreviated as PET) is preferably used.

The polyester which is first supplied in the process of the present invention has an intrinsic viscosity of at least 0.40, preferably from 0.50 to 1.20, more preferably from 0.60 to 1.00. The term "intrinsic viscosity" used herein means the value as measured at 20°C on a solution of the polyester resin in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane in a 60:40 weight ratio, and is hereinafter abbreviated as IV.

The titanium dioxide used in the present invention is preferably of the rutile and/or anatase type. The titanium dioxide has an average particle size of 0.1 to 0.5 µm. Particles whose size is outside this range will not provide a satisfactory degree of whiteness or hiding power. The average particle size of the titanium

dioxide can be measured by any known method such as electron microscopy or a precipitation technique.

The titanium dioxide particles used in the present invention have been surface treated with an aluminum compound and/or a silicon compound. The surface treatment is performed in order to impart affinity for the polyester resin by treating the particles of titanium dioxide with an aluminum compound (e.g. alumina) and/or a silicon compound (e.g. silica) that has an oxygen or hydroxyl bond. After this treatment, the titanium dioxide may be subjected to further surface treatments with metal soaps (e.g. zinc stearate, magnesium stearate and sodium palmitate), surfactants (e.g. alkylene oxide derivatives, aliphatic acid esters of polyhydric alcohols, quaternary ammonium salts, alkyl sulfate esters and amino acids), silane and titanium coupling agents, silicone oil, alcohols (e.g. methanol and ethanol) and polyhydric alcohols (e.g. ethylene glycol).

The titanium dioxide used in the present invention has a water content of no more than 0.5%. The water content of titanium dioxide can be measured by the following method specified in "Pigment Test Methods, Section 21" under JIS K 5101: A prescribed amount of a sample is correctly measured in a pre-dried flat-bottom weighing bottle (50 ml) and spread on its bottom as uniformly as possible as a layer; after stoppering the bottle, its weight is measured; the stopper is then removed and both the bottle and the stopper are dried in a dryer held at 110°C for 2 hours; they are transferred into a desiccator and left to cool; after replacing the stopper on the bottle, its weight is measured to determine the weight loss; the water content of the sample, K (%), can be calculated by the following formula: $K = \frac{L}{S} \times 100$ where L is the weight loss (g) and S is the mass of the sample (g). For the purposes of the present invention, it suffices that the water content of titanium dioxide is 0.5% or less when measured just prior to kneading with the polyester.

If the water content of the titanium dioxide is higher than 0.5%, the polyester resin, when mixed with the titanium dioxide in the molten state, will undergo hydrolysis by the water in the latter. Another reason why titanium dioxide containing more than 0.5% water should not be used is that the particles with such a high water content will readily agglomerate to form coarse particles.

The titanium dioxide is surface-treated in order to provide it with affinity for the polyester resin. The surface treatment is such that the water content of the titanium oxide is held at no more than 0.5%.

When the titanium dioxide and polyester resin are supplied into a continuous kneading extruder in which the two components are kneaded in the molten state, the concentration of the titanium dioxide lies is from 20 to 70 wt%.

Titanium dioxide may be used in combination with other pigments in the process of the present invention, such as barium sulfate, silica, alumina, talc and calcium carbonate, either on their own or as admixtures.

Other additives in common use, such as brighteners, dyes, uv absorbers, antistats and antioxidants, may also be incorporated in amounts that will not be detrimental to the object of the present invention.

Polymeric materials other than polyesters can also be added; examples are polyolefins such as polyethylene and polypropylene.

The polyester resin and titanium dioxide supplied to the continuous kneading extruder are subjected to a kneading action in a zone equipped with kneading disks or rotor blades. In the kneading zone, high temperatures occur because of the heat generated by the shearing action so the barrel is preferably cooled with water.

After the initially supplied polyester is blended with the titanium dioxide, an additional feed of a polyester resin is supplied to the continuous kneading extruder. The IV of the additionally supplied polyester resin is not limited to any particular value, but the IV of the initially supplied polyester resin and that of the additionally supplied polyester resin are preferably selected to produce maximum kneading effects while preventing the deterioration of the resins. The IV of the initially supplied polyester resin may or may not be the same as that of the additionally supplied polyester resin.

The process of the present invention is especially useful in the production of polyester resin compositions having high concentrations of titanium dioxide, so the amount of the additional feed of the polyester resin is determined such that the finally obtained resin composition has a titanium dioxide concentration, for example, in the range of 10 to 50 wt%.

Whether supplied initially or additionally, the polyester resin used in the present invention may be charged into the continuous kneading extruder either in a solid or molten state. The additionally supplied polyester is preferably added in a state because this permits the temperature of the resin to drop when melted.

The continuous kneading extruder may be furnished with a kneading unit (e.g. a kneading disk) or an air vent that come into play in the period from the supply of the additional charge of polyester resin to the delivery of the resin composition.

By the process of the present invention a polyester resin composition having a high concentration of titanium dioxide uniformly dispersed therein emerges from the continuous kneading extruder. The composition, as it emerges from the extruder, may be fed into a film forming apparatus either directly or after having been shaped into chips. In the latter case, the chips are preferably formed into a film after they are subjected to a heat treatment as described in Japanese Patent Application (OPI) Nos. 184538/1986 and 186957/1986.

Films can be produced by any known method such as the one described in Japanese Patent Application (OPI) No. 118746/1986. The film thus produced is useful as a reflective photographic support. For the preparation of reflective photographic materials using this film, see prior patents such as Japanese Patent Application No. 118746/1986.

The following Example further illustrates the present invention.

EXAMPLE

Various types of titanium dioxide were blended with a polyethylene terephthalate resin in a co-rotating twin-screw kneading extruder (Model PCM- 65 of Ikegai Iron Works, Ltd.) at a die temperature of 280 °C with the screws rotating at 150 rpm to produce a throughput of 100 kg/h.

The type of titanium dioxide used are defined in Table 1.

Table 1

	Sample No.	Crystal form	Average particle size (μm)	Surface treatment	Water content (%)
Present invention	A	anatase	0.3	Al_2O_3 0.2% SiO_2 0.2% ethylene glycol 0.3%	0.18
	B	rutile	0.2	Al_2O_3 0.3% SiO_2 0.3%	0.22
Comparison	C	anatase	0.3	not applied	0.37
	D	anatase	0.3	Al_2O_3 4.0% polyvinyl alcohol 0.3%	0.55

The kneading conditions are set forth in Table 2, in which Nos. 1 and 2 are samples used according to the present invention and Nos. 3 - 7 are comparative samples.

The TiO_2 containing polyester compositions that had been passed through the kneading stage were discharged from the twin-screw kneading extruder, cooled with water and shaped into square pellets (3 mm x 3 mm x 3 mm).

A pellet was taken from each sample, melted on a glass plate, spread in a thin film and observed under a microscope (X100) to count the number of coarse (≥ 20 μm) particles. Five measurements were made and their average was taken.

The results are shown in Table 2. The colour of the pellets obtained was measured with TC-1500DX, a colour difference meter of Tokyo Denshoku K.K. The results of colour measurement are expressed by L, a and b according to Hunter's color difference formula; only the values of b denoting yellowness are given in Table 2. The greater the positive value of b, the more intense the yellowness of the sample under test.

Table 2

	No.	TiO_2	Initially supplied PET's IV	Additionally supplied PET's IV	TiO_2 intermediate concentration (%)	TiO_2 final concentration (%)	No. of coarse particles	b value of pellets
Present invention	1	A	0.70	0.60	35	20	1.2	1.5
	2	B	0.84	0.65	65	15	1.8	2.1
Comparison	3	C	0.64	0.69	35	17	6	4.2
	4	C	0.64	0.64	40	20	16	2.9
	5	B	0.30	0.65	60	15	21	2.3
	6	A	0.70	0.60	80	20	8	3.2
	7	D	0.70	0.60	40	20	12	2.9

As Table 2 shows, the process of the present invention successfully produced TiO_2 containing polyester resin compositions that featured a markedly improved uniformity in the dispersion of TiO_2 particles and which afforded increased whiteness with a reduced degree of yellowness.

Pellets of sample Nos. 1 and 2 were heated at 220°C for 6 hours at 133 Pa (1 Torr) and fed to an extruder at 290°C, from which the extrudates were brought into contact with a rotating chill drum to form amorphous sheets 1.1 mm thick. Each of the sheets was stretched first longitudinally at a draw ratio of 3.0 at 100°C, then transversely at a draw ratio of 3.0 at 110°C. The drawn sheets were heat-set at 200°C, cooled and wound up. The thus prepared films had a thickness of 125 µm and were white and opaque. The drawing and shaping operations could be performed in a continuous stable manner. The films had a sufficient degree of whiteness and opacity to be useful as reflective photographic supports.

Claims

1. A process for producing a polyester resin composition by first supplying a polyester resin having an intrinsic viscosity of at least 0.40 and titanium dioxide having an average particle size of 0.1 to 0.5 µm and a water content of no more than 0.5%, the particles of which have been surface-treated with an aluminum compound and/or a silicon compound, to a continuous kneading extruder, kneading them in the molten state such that the concentration of titanium dioxide is from 20 to 70 wt%, and then supplying an additional charge of the polyester resin to give a desired concentration of the titanium dioxide.

2. A process according to claim 1 wherein said polyester resin is polyethylene terephthalate, polyethylene 2,6-dinaphthalate, polypropylene terephthalate or polybutylene terephthalate.

3. A process according to claim 2 wherein said polyester resin is polyethylene terephthalate.

4. A process according to any one of claims 1 to 3 wherein the first supplied polyester resin has an intrinsic viscosity from 0.50 to 1.20.

5. A process according to claim 4 wherein the first supplied polyester resin has an intrinsic viscosity from 0.6 to 1.00.

6. A process according to any one of claims 1 to 5 wherein said aluminum compound is alumina.

7. A process according to any one of claims 1 to 5 wherein said silicon compound is silica.

8. A process according to any one of claims 1 to 7 wherein the concentration of said titanium dioxide in the final polyester resin composition is from 10 to 50 wt%.

Revendications

1. Procédé de fabrication d'une composition de résine polyester dans lequel on fournit **en premier une** résine polyester ayant une viscosité intrinsèque d'au moins 0,40 et du dioxyde de titane ayant une taille particulaire moyenne de 0,1 à 0,5 µm et une teneur en eau ne dépassant pas 0,5%, dont les particules ont été traitées à leur surface avec un composé d'aluminium et/ou un composé de silicium, dans une extrudeuse à pétrissage continu, on les pétrit à l'état fondu de manière que la concentration de dioxyde de titane soit de 20 à 70% en poids, puis on fournit une charge additionnelle de la résine polyester pour donner la concentration désirée de dioxyde de titane.

2. Procédé selon la revendication 1 dans lequel ladite résine polyester est le téréphtalate de polyéthylène, le 2,6-dinaphtalate de polyéthylène, le téréphtalate de polypropylène ou le téréphtalate de polybutylène.

3. Procédé selon la revendication 2 dans lequel ladite résine polyester est le téréphtalate de polyéthylène.

4. Procédé selon l'une quelconque des revendications 1 à 3 dans lequel la résine polyester fournie en premier a une viscosité intrinsèque de 0,50 à 1,20.

5. Procédé selon la revendication 4 dans lequel la résine polyester fournie en premier a une viscosité intrinsèque de 0,6 à 1,00.

6. Procédé selon l'une quelconque des revendications 1 à 5 dans lequel ledit composé d'aluminium est l'alumine.

7. Procédé selon l'une quelconque des revendications 1 à 5 dans lequel ledit composé de silicium est la silice.

8. Procédé selon l'une quelconque des revendications 1 à 7 dans lequel la concentration dudit dioxyde de titane dans la composition de résine polyester finale est de 10 à 50% en poids.

Patentansprüche

1. Verfahren zur Herstellung einer Polyesterharzmasse, bei dem man zunächst ein Polyesterharz einer Intrinsic-Viskosität von mindestens 0,40 und Titandioxid einer durchschnittlichen Teilchengröße von 0,1 bis 0,5 µm und eines Wassergehalts von nicht mehr als 0,5 %, dessen Teilchen mit einer Aluminiumverbindung und/oder einer Siliciumverbindung oberflächenbehandelt wurden, einem kontinuierlich arbeitenden Knetextruder zuführt, beide in aufgeschmolzenem Zustand derart verknetet, daß die Konzentration an Titandioxid 20 bis 70 Gew.-% beträgt, und schließlich eine weitere Charge Polyesterharz zuführt, um eine gewünschte Titandioxidkonzentration zu erreichen.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß das Polyesterharz aus Polyethylenterephthalat, Polyethylen-2,6-dinaphthalat, Polypropylenterephthalat oder Polybutylenterephthalat besteht.

3. Verfahren nach Anspruch 2, **dadurch gekennzeichnet**, daß das Polyesterharz aus Polyethylenterephthalat besteht.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß das zunächst zugeführte Polyesterharz eine Intrinsic-Viskosität von 0,50 bis 1,20 aufweist.

5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet**, daß das zunächst zugeführte Polyesterharz eine Intrinsic-Viskosität von 0,6 bis 1,00 aufweist.

6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß die Aluminiumverbindung aus Aluminiumoxid besteht.

7. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß die Siliciumverbindung aus Siliciumdioxid besteht.

8. Verfahren nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet**, daß die Konzentration an Titandioxid in der fertigen Polyesterharzmasse 10 bis 50 Gew.-% beträgt.